

Using Surface Water Application to Reduce 1,3-Dichloropropene Emission from Soil Fumigation

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ABSTRACT

High emissions from soil fumigants increase the risk of detrimental impact on workers, bystanders, and the environment, and jeopardize future availability of fumigants. Efficient and cost-effective approaches to minimize emissions are needed. This study evaluated the potential of surface water application (or water seal) to reduce 1,3-dichloropropene (1,3-D) emissions from soil (Hanford sandy loam) columns. Treatments included dry soil (control), initial water application (8 mm of water just before fumigant application), initial plus a second water application (2.6 mm) at 12 h, initial plus two water applications (2.6 mm each time) at 12 and 24 h, standard high density polyethylene (HDPE) tarp, initial water application plus HDPE tarp, and virtually impermeable film (VIF) tarp. Emissions from the soil surface and distribution of 1,3-D in the soil-gas phase were monitored for 2 wk. Each water application abruptly reduced 1,3-D emission flux, which rebounded over a few hours. Peak emission rates were substantially reduced, but total emission reduction was small. Total fumigant emission was 51% of applied for the control, 46% for initial water application only, and 41% for the three intermittent water applications with the remaining water treatment intermediate. The HDPE tarp alone resulted in 45% emission, while initial water application plus HDPE tarp resulted in 38% emission. The most effective soil surface treatment was VIF tarp (10% emission). Surface water application can be as effective, and less expensive than, standard HDPE tarp. Frequent water application is required to substantially reduce emissions.

METHYL BROMIDE (MeBr) is being phased out internationally as a stratospheric ozone depleting compound. Other fumigants, such as 1,3-dichloropropene (1,3-D), chloropicrin, and metam sodium (methyl isothiocyanate [MITC] generator), are being used as alternatives to MeBr for soil fumigation. Uses of fumigants are regulated primarily based on their toxicology properties and air emissions. Minimizing emissions will be critical to protecting workers, bystanders, and the environment, and to maintaining practicable use of alternative fumigants to MeBr for agricultural production.

Emissions from soil fumigation are affected by soil texture and water content, weather, and surface barriers as well as fumigant properties. Methods to reduce fumigant emissions include application methods such as chemigation (through drip irrigation), chemical remediation (e.g., use of thiosulfate to degrade fumigants), and surface barriers (plastic tarps and water seals) (Yates et al., 2002). Chemigation was shown to reduce fumigant

emissions compared to shank injections in some cases (Gan et al., 1998b) but not in others (Sullivan et al., 2004). Chemical remediation at the surface (e.g., using thiosulfate) can reduce emissions substantially by reacting with and destroying the fumigants at the surface (Gan et al., 1998a). This method has not yet been tested in the field or evaluated economically. Surface plastic tarp (mulch) reduces fumigant emissions, depending on the chemical, and is generally expensive (about \$2000 per ha for purchase, placement, removal, and disposal of high density polyethylene [HDPE] tarps over shank applications). High density polyethylene film is a poor barrier for 1,3-D, but is more effective with MeBr and chloropicrin (Wang et al., 1999; Papiernik and Yates, 2002). Plastic tarp was found to improve pest treatment of surface soil—especially weed control (Shem-Tov et al., 2005). Use of virtually impermeable film (VIF) is more effective in reducing 1,3-D as well as other fumigant emissions than standard HDPE tarp (e.g., Noling, 2002; Thomas et al., 2004, 2006; Wang et al., 1999), but this method is even higher cost and practical application methods that preserve the high barrier characteristics are still being developed. High surface soil water content was found to create a more effective barrier to 1,3-D movement than HDPE (Gan et al., 1998b; Thomas et al., 2003).

Surface water seal (applying water uniformly to soil surface) is a technique that has shown potential to reduce fumigant emissions by forming a high water content layer at the surface that serves as a diffusion barrier. Fumigant diffusion rate in the liquid phase is much lower than through the gas phase. High soil water content and slight compaction at the soil surface reduces emissions also by reducing air-filled pore space. Water application to surface soil in column studies and small plots showed substantial reduction of MeBr emissions especially when combined with use of plastic tarp (Jin and Jury, 1995; Wang et al., 1997). More recent field trials studied use of surface water sprinkler irrigation (water seal) to reduce MITC emissions and found that intermittent water sealing was particularly effective to minimize off-gassing during night time periods when atmospheric dispersion conditions were relatively poor (Sullivan et al., 2004). This technique will usually cost less than using plastic tarps in areas where irrigation water is available, especially on farms where sprinkler systems are used.

The objective of this study was to determine the potential of using surface water applications to reduce 1,3-D emissions in soil columns. Although soil columns

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Abbreviations: 1,3-D, 1,3-dichloropropene; HDPE, high density polyethylene; MeBr, methyl bromide; MITC, methyl isothiocyanate; VIF, virtually impermeable film.

cannot fully represent field conditions, they allow us to efficiently test several treatments. Our purpose was to identify the effective treatments to reduce fumigant emissions for further tests in field trials.

MATERIALS AND METHODS

Soil, Chemicals, and Plastic Materials

A Hanford sandy loam soil (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) was collected from the surface (0–30 cm depth) at the San Joaquin Valley Agricultural Sciences Center, USDA-ARS, Parlier, California. The soil had a pH of 8.5 and electrical conductivity (EC) of 0.80 dS m⁻¹ in 1:1 soil water extracts, a cation exchange capacity (CEC) of 6.8 cmol_c kg⁻¹, and an organic matter content of 0.72%. At 33-kPa suction, the soil water content is about 17% (w/w) (Skaggs et al., 2004). The soil was air-dried to a water content of about 5% (w/w), sieved through a 4-mm screen, and mixed before packing the soil columns. *Cis*-1,3-dichloropropene (purity of 98.9%) was provided by Dow AgroSciences Company (Indianapolis, IN). Ethyl acetate (pesticide grade), hexane (pesticide grade), and sodium sulfate anhydrous 10–60 mesh (ACS grade) were obtained from Fisher Scientific (Hampton, NH). High density polyethylene film and VIF “Hytibarrier” were obtained from TriCal (Hollister, CA) and Klerk’s Plastic Products (Richburg, SC), respectively.

Soil Column Experiment

Soil was packed into close-bottomed stainless steel columns (63.5-cm height × 15.5-cm i.d.). Soil was packed to a total depth of 61.5 cm leaving the top 2 cm empty in the column and allowing surface water application when needed. The columns were packed in 5-cm increments to a uniform bulk density of 1.4 g cm⁻³. Sampling ports for soil gases were installed at depths of 0 (under plastic tarp when applied), 10, 20, 30, 40, 50, and 60 cm below the soil surface. A Teflon-faced silicone rubber septum (3 mm thick; Supelco, Bellefonte, PA) was installed in each sampling port. The septum was replaced with a new one after each sampling. A Teflon tube attached to the inside of each sampling port extended to the center of the column.

For emission measurement, a flow-through gas sampling chamber (4.5 cm deep with the same diameter as the soil column) was placed on the top of the soil column and sealed to the column with a sealant-coated aluminum tape to avoid any gas leakage. After the whole column was assembled and treatment was applied, a continuous flow rate of 110 ± 10 mL min⁻¹ through the chamber was maintained by vacuum. The chamber inlet port was sized such that pressure inside the chamber should be no more than 0.6% below atmospheric pressure. A flow meter was used to adjust the air-flow rate after sampling tubes were replaced and occasionally between sampling times. The flow rate usually stabilized within 5 min to the set range. The column experiments were conducted at laboratory room temperature (22 ± 3°C). Monitoring and sampling were done for 2 wk.

One-hundred microliters of liquid *cis*-1,3-D (120 mg) was injected into the column center at the 30-cm depth through an injection port connected to a Teflon tube extending to the center of the column. Similar behavior of degradation, emission, and plastic tarp permeability (e.g., HDPE) was observed between the isomers, that is, *cis*- and *trans*-1,3-D (e.g., Gan et al., 1999; Wang et al., 1999; Papiernik and Yates, 2002). *Cis*-1,3-dichloropropene was chosen in this study to predict what will happen when the commercial 1,3-D fumigant Telone II (mixture of the isomers) is applied to soil. Some

studies showed that *cis*-1,3-D diffused slightly faster than *trans*-1,3-D through HDPE film or soil (e.g., Noling, 2002; Thomas et al., 2003).

To evaluate the potential of using surface water applications to reduce 1,3-D emissions, the following treatments were applied to soil columns:

- A. Dry soil (control).
- B. Initial water application by spraying 148 g per column, equivalent to an 8-mm depth, of water to the soil surface just before the fumigant was injected. This amount of water can wet a 5-cm depth of soil to its water holding capacity.
- C. Same as Treatment B followed by a second water application of 49 g per column (2.6-mm depth) at 12 h after fumigant injection.
- D. Same as Treatment C followed by a third water application of 49 g per column (2.6-mm depth) at 24 h after fumigant injection.
- E. Dry soil with HDPE tarp.
- F. Initial water application (Treatment B) plus HDPE tarp.
- G. Dry soil with VIF tarp.

For surface water application, tap water was quickly applied (within 5 min) to the soil surface using a spray bottle. Eight millimeters of water usually disappeared from the surface within 20 min reflecting a fast infiltration rate. For water applications at 12 and 24 h, the top chamber was removed to spray water onto the soil surface. This resulted in loss of the fumigant from the headspace. The total volume of air in the headspace above the soil surface was 1.22 L. The air-flow rate created one headspace air exchange every 11 min or about three exchanges each 30-min sampling interval. The effect of the chamber removal on the 1,3-D sampling and estimate of emissions was adjusted, that is, measured emission rate for the first sample after water application was increased by 60% to correct for fumigant loss due to removal of the chamber. After the first ORBO tube was replaced, measured emissions should not have been affected by the removal of the chamber. When used, plastic tarps were sealed to the top edge of the stainless steel columns using silicone sealant to minimize leakage.

Treatments A through D were repeated. Because the same trends and similar results were obtained for all the repeated treatments (duplicate results are reported in Table 1), treatments with plastic tarps were not repeated.

Sampling and Analysis

The ORBO 613, XAD 4 80/40mg (Supelco) tubes were connected to the outlet of the top air chambers to adsorb fumigants in the headspace. We tested that under the studied conditions, these tubes can adsorb 1,3-D as efficiently as standard charcoal tubes (e.g., ORBO 32; Supelco) that have been used to adsorb 1,3-D in other studies. During the day the tubes were replaced every 30 min for the first 48 h, every 1 h throughout the first week, and every 2 h the second week. The time the fumigant was injected into the soil column was considered time zero. At night, a chain of the tubes (2–6) was connected to ensure trapping of all emissions, and the last ORBO tube in the chain always showed non-detection, which proves that all 1,3-D had been collected.

The ORBO tubes were extracted immediately or frozen for up to 14 d for later extraction. After breaking each tube, all materials were transferred into a 10-mL clear headspace vial. Five milliliters of hexane were added to the vial and the vial was then shaken for 2 h. After settling, a portion of the solvent in the vial was transferred to a 2-mL amber gas chromatography (GC) vial. The GC vials were stored in a freezer before

Table 1. Peak flux and 1,3-D emissions from soil column treatments as compared to the control.

Treatment†	Peak flux $\mu\text{g m}^{-2} \text{s}^{-1}$	1,3-D cumulative emission‡			
		24 h	48 h	72 h	336 h
		% of control			
Control§ (% of applied)	15.7	13.8 (1)	26.2 (1)	34.2 (<1)	50.6 (2)
Initial water (8 mm)	10.3	63 (6)	75 (3)	81 (3)	91 (1)
Initial water (8 mm) + 2.6 mm at 12 h	8.2	47 (5)	63 (4)	71 (8)	88 (1)
Initial water (8 mm) + 2.6 mm at 12 h + 2.6 mm at 24 h	7.5	45 (6)	51 (4)	58 (5)	81 (4)
HDPE	10.2	69	75	77	87
Initial water (8 mm) + HDPE	8.6	36	51	58	74
VIF	1.3	5	8	9	19

† HDPE, high density polyethylene; VIF, virtually impermeable film.

‡ Values in parentheses are standard deviations of duplicate column measurements.

§ Data for the control are reported as the % of applied.

analysis. Fumigants in the extracts were analyzed by a GC–mass spectrometry (MS) system (6890 Network GC system, 7683 AutoInjector, and 5973 Inert Mass Selective Detector; Agilent Technologies, Palo Alto, CA). A DB-VRX capillary column (30-m length \times 0.25-mm i.d. \times 1.4- μm film thickness; Agilent Technologies) was used. The injected volume was 2 μL splitless. The carrier gas (He) flow rate and inlet temperature were set at 1.3 mL min^{-1} and 140°C, respectively. The mass selective detector temperatures were set as follows: transfer line 260°C, source 230°C, and quad 150°C. The oven temperature program was as follows: initially 45°C, increasing at 2.5°C min^{-1} to 75°C, and then at 99°C min^{-1} to 110°C and held for 7 min. The retention time for *cis*-1,3-D was 8.6 min.

For determining fumigant concentration in soil-gas phase, 0.5-mL volume of soil gas was withdrawn from the sampling ports with a gas-tight syringe at times of 3, 6, 12, 24, 36, and 48 h, and 3, 4, 7, 9, 11, and 14 d after fumigant injection. The gas sample was injected into a 21-mL clear headspace vial and the vials were crimp-sealed immediately with an aluminum caps and Teflon-faced butyl-rubber septum (Supelco). This method was quantitative and reproducible (Gan et al., 1997). To avoid moisture effect on the fumigant stability, 0.2 g sodium sulfate was added to each vial before sample injections. If analysis could not be performed immediately, the vials were stored in an ultra freezer at a temperature of -44°C . All samples were analyzed within 72 h, a stable period of time for fumigants under laboratory conditions (Guo et al., 2004b). The analysis was performed using a GC- μECD (Agilent Technologies 6890N Network GC system with a micro electron capture detector) and an automated headspace sampler (Agilent Technologies G1888 Network Headspace Sampler) system. A DB-VRX capillary column was used with the same dimension as the fumigant analysis mentioned above. Conditions for the headspace autosampler were: equilibration temperature, 100°C; equilibration time, 2 min; and sample loop, 1 mL. The GC carrier gas (He) flow rate, inlet temperature, and detector temperature were set at 2.0 mL min^{-1} , 150°C, and 300°C, respectively. The oven temperature program was the same as the GC–MS system described above.

Upon termination of the experiment, soil samples from each column were taken at 10-cm depth intervals, and soil water content and residual 1,3-D in the soil were determined. The extraction procedure for soil samples basically followed Guo et al. (2003). An equivalent dry weight of 8 g of soil was added to a 21-mL clear vial that contained Na_2SO_4 (amount depended on soil water content at a 7:1 ratio of Na_2SO_4 to water). Eight milliliters of ethyl acetate were added to the vial. The vial was crimp-sealed with aluminum caps and a Teflon-faced butyl-rubber septum. After the vials were incubated at 80°C in a water bath over night (approximately 18 h), the supernatant was settled and a portion was transferred into a 2-mL amber GC vial for fumigant analysis using the GC–MS as described

above. The vials were preserved in the freezer when analysis could not be completed immediately.

RESULTS AND DISCUSSION

Surface Emissions

Emission Flux

The emission fluxes of 1,3-D from the column treatments are shown in Fig. 1. In the control (dry soil), flux increased rapidly beginning 3 h after fumigant injection, peaked (approximately 16 $\mu\text{g m}^{-2} \text{s}^{-1}$) at about 15 h, and gradually decreased thereafter. The initial 8 mm of water applied just before fumigant injection reduced the peak flux to 10 $\mu\text{g m}^{-2} \text{s}^{-1}$ and delayed emissions 1 to 2 h compared to the control. Additional water application of 2.6 mm at 12 h abruptly reduced 1,3-D emission flux to below 3 $\mu\text{g m}^{-2} \text{s}^{-1}$, but the volatilization rates quickly rebounded to approach those without this second water application. The estimated impact of the emission chamber removal during water application on the observed abrupt reduction was corrected as indicated in the previous section when plotting the data. Because nearly 3 air volume exchanges occurred during the first sample interval (30 min), following measurements were not adjusted. Treatment D, which included the third water application (2.6 mm), repeated this rapid reduction and rebound at 24 h. The abrupt reduction in emission flux reflects the immediate impact of surface water application. The rebound in 1,3-D emission rates nearly approached those treatments without surface water additions by 48 h. This indicates that frequent applications of surface water may be needed to maximize the effect of surface water application on emission reductions. Gan et al. (1998b) found that application of 15 mm of water dripped slowly (2 mL min^{-1}) on the soil surface after 1,3-D was injected at 20-cm depth in soil columns substantially reduced 1,3-D emission and the emission reduction was even more effective when an emulsified formulation of 1,3-D was applied.

Use of HDPE tarp showed a similar degree of emission reduction as the initial surface water application. Previous laboratory and field studies have shown that HDPE is not effective in reducing 1,3-D volatilization because of its high permeability to 1,3-D (e.g., Gan et al., 1998b; Papiernik and Yates, 2002; Thomas et al., 2006).

Initial water application plus HDPE tarp provided additional emission reduction over the first 48 h. Similar

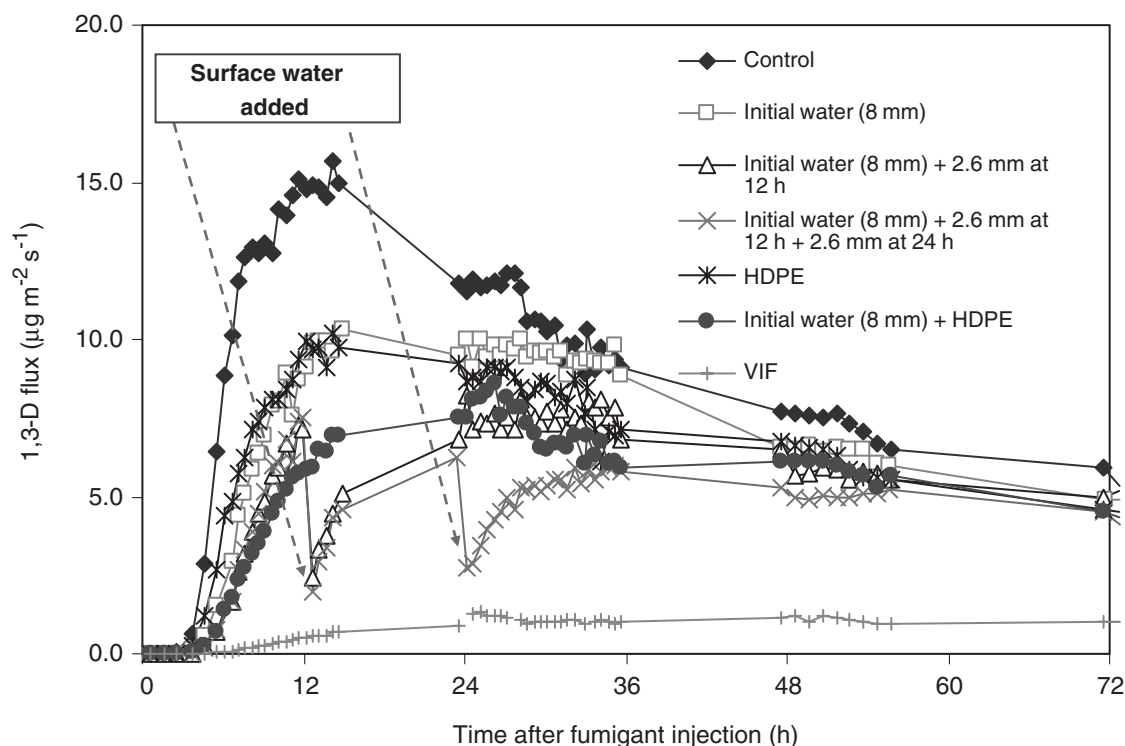


Fig. 1. 1,3-Dichloropropene (1,3-D) emission fluxes from soil column treatments.

results were obtained for MeBr when water application plus HDPE tarp reduced MeBr emissions much more efficiently than HDPE tarp alone in soil columns and small plots (Jin and Jury, 1995; Wang et al., 1997). This treatment might be even more effective on reducing emissions in the field where diurnal temperature fluctuations cause periodic water evaporation and condensation under the tarp, which helps maintain the surface soil moisture as an effective barrier to fumigants.

The maximum reduction of 1,3-D emissions from our treatments was with VIF tarp, which showed very low emission rates ($<1.5 \mu\text{g m}^{-2} \text{s}^{-1}$). Although VIF had extremely low emissions under laboratory conditions, damage to the film during field application and difficulties in joining (gluing) VIF sheets together may result in significantly greater emissions under field conditions than we observed in the column studies.

All the treatments except VIF had similar emissions beyond 72 h (data not shown). Most treatments showed very low emission rates ($0.0\text{--}0.5 \mu\text{g m}^{-2} \text{s}^{-1}$) at the end of the experiments (2 wk).

Total Emissions

The cumulative emissions from the column treatments during the 2-wk experimental period are shown in Fig. 2. The closed bottom of the soil columns would limit downward movement of fumigant, which may result in more upward movement compared to longer columns. The relative difference among soil surface treatments should not be affected significantly. For the total 2 wk, the emission percentages of total applied were 51% for the control, 46% for the initial water application, 45% for the initial water plus a second water application

(2.6 mm) at 12 h, 41% for the initial water plus water applications at 12 h and 24 h, 45% for HDPE tarp only, 38% for the initial water application plus HDPE tarp, and 10% for VIF tarp. The VIF was clearly the most effective barrier to reduce 1,3-D emissions among all the treatments. The three water applications were more effective in reducing total emissions than those with fewer water applications and the HDPE tarp with the initial water application was more effective than the HDPE

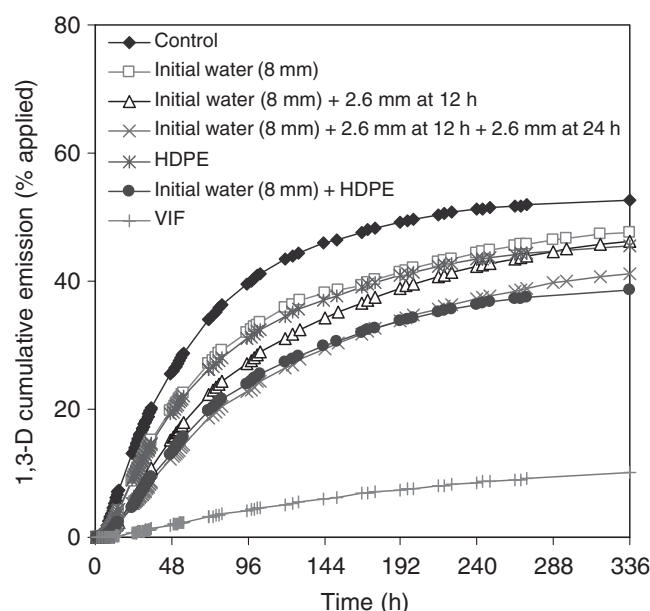


Fig. 2. Cumulative 1,3-dichloropropene (1,3-D) emission loss from soil column treatments.

tarp alone, which indicates the important role of soil water in 1,3-D emission reduction.

To evaluate emission reduction of treatments over time, cumulative emission of each treatment is compared to that of the control (Table 1). All the treatments, especially water applications that were applied during the first 24 h, showed greater relative emission reduction in the first few days than the total emission over the 2-wk period. Initial water application, initial water followed by the two intermittent water applications at 12 h and 24 h, initial water plus HDPE, and VIF tarp reduced emissions about 25, 49, 49, and 92% respectively, compared to the control, for the first 48 h, and these values decreased to 9, 19, 26, and 81%, respectively, for the 2-wk period. The relative emission reduction for HDPE tarp alone was 25 and 13% for the first 48 h and the 2-wk period, respectively.

These results indicate that surface water applications alone and in combination with HDPE tarp are effective in reducing early emissions, and thereby reducing risks to workers and bystanders during fumigation. Water application just before fumigant injection also showed a lag period of time before emission rates significantly increased compared to the control. Reducing peak flux is important for fumigants for which acute toxicity or odor (e.g., chloropicrin) is the primary concern. Reducing overall emissions is also desired for fumigants, such as 1,3-D, when total exposure (chronic toxicity) is also a concern, or for all fumigants where impact of air-borne organic compounds contribute to air quality (ozone) problems.

Results from our column tests show that the intermittent water applications reduced 1,3-D emissions equally or more effectively than HDPE tarp (Fig. 1 and 2; Table 1). This is not surprising considering the known high permeability of HDPE to 1,3-D. The diffusion rate of 1,3-D dramatically reduced as soil water content increased and as a result, emission of 1,3-D was also reduced and was minimal from the near-water-saturated soil (Thomas et al., 2003).

The cost for using standard HDPE tarp over shank applications is about \$2000 ha⁻¹ (\$800 acre⁻¹) in the San Joaquin Valley of California. This estimate includes cost of the materials (tarp and glue: \$1240 ha⁻¹), application (\$470 ha⁻¹), and removal and disposal (\$270–\$440 ha⁻¹). For surface water applications using a sprinkler system, cost estimate for a total 25 mm of water (about twice the amount of water used in the column tests) application is in the range of \$100 to 700 ha⁻¹ (\$40–280 acre⁻¹), depending on whether the grower owns or rents the sprinkler system. This estimate is based on an estimated water cost of \$0.04 m⁻³ (\$10 per ha for a 25-mm application), 5 worker-h per ha for sprinkler installation and removal (<\$80 per ha), and sprinkler system rental/delivery cost of \$600 per ha (depending greatly on the number of times the system is moved and reused). The overall cost of using water is substantially less than using plastic tarp. Thus, using water seal to reduce emissions has a great potential where irrigation water is available. Irrigation system capacity may limit the area that can be fumigated each day.

Two practices may reduce emissions beyond those achieved in these tests. Emission reductions depend on high soil water content in the surface soil. Therefore, very frequent small irrigations may further reduce both peak and total fumigant emission. Since the sprinkler system must be in the field for the treatment, applying small, frequent irrigations is possible. The second technique is to promote the degradation rate of the fumigant in soil surface, such as with the use of thiosulfate or thiourea (Wang et al., 2000; Zheng et al., 2004). A concern with both practices is if fumigant concentration is reduced significantly near the soil surface that resulted in the reduction in dosage exposure (concentration × time) and may reduce fumigation efficacy near the surface. Reduced emissions and the decreased diffusion rate of fumigants in soils with high water content were observed by Thomas et al. (2003). Further investigations are necessary on how to maintain fumigation efficacy while reducing emissions using water or chemicals that are delivered with water.

The results of surface water application on reducing 1,3-D emissions observed in this study may not apply to other fumigants with different chemical properties. Other fumigants may exhibit different emission patterns, such as metam sodium as a generator of MITC (Merricks, 2002). To maximize emission reduction, surface water applications may be different from what we observed for 1,3-D. High density polyethylene tarp provides more resistance to MeBr and chloropicrin than to 1,3-D. Thus, the relative effect of water application or plastic tarps on reducing fumigant emissions will be different for various chemicals. For instance, an 8-mm initial water application with HDPE tarp in our column experiment reduced emissions an additional 8% of applied from that achieved with tarp alone. Jin and Jury (1995) showed that application of 4 mm of water plus 1-mil HDPE tarp reduced MeBr emission an additional 25% of applied. The combination of water application with HDPE tarp on emission reduction bears further investigation for different fumigants.

1,3-Dichloropropene Concentrations in Soil Gas Phase

The distribution of 1,3-D in the soil-gas phase over time is shown in Fig. 3. Note that for the tarped treatments, fumigant concentration at the soil surface (depth = 0 cm) was sampled under the tarp. The main difference observed in 1,3-D concentrations in soil gas was between the VIF tarp treatment and others. The VIF tarp was able to retain much higher 1,3-D concentrations in the soil-gas phase than other treatments, especially at later times (after 24 h). At the first sample time (3 h), all treatments had essentially the same fumigant concentration distribution. The fumigant concentration reached the highest level at the bottom sampling port at or before 24 h for all treatments. After this time, fumigant was dispersed throughout the lower column fairly evenly due to the closed bottom. The concentration of 1,3-D in soil-gas phase decreased to below 0.1 mg L⁻¹ by the end of the experiment in all of the columns

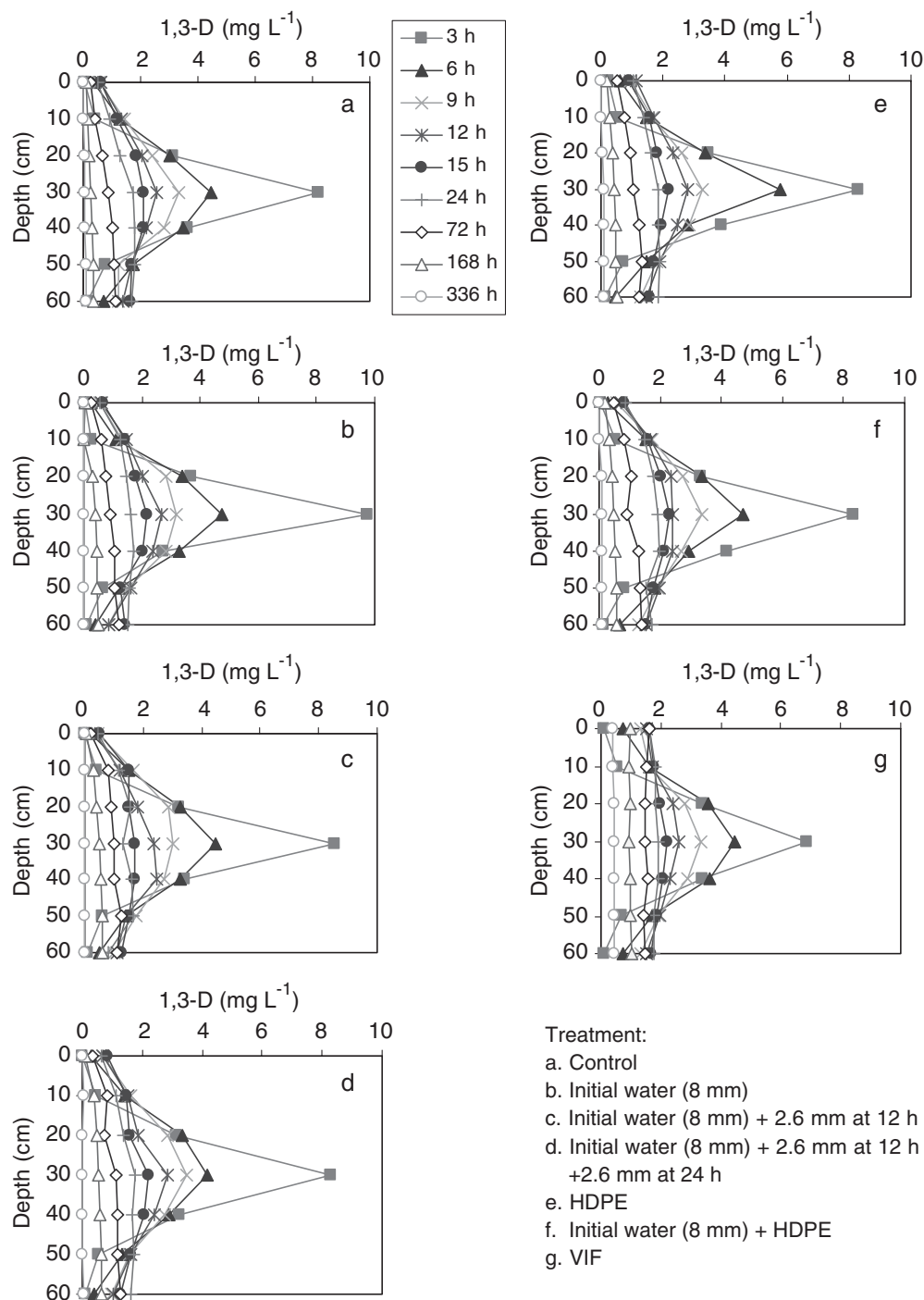


Fig. 3. Distribution of 1,3-dichloropropene (1,3-D) in the soil-gas phase from soil column treatments.

except the VIF treatment where about 0.4 mg L^{-1} 1,3-D was detected throughout the profile. The VIF tarp reduced emissions the most and maintained elevated fumigant concentrations in soil profile for the longest time. This may imply that substantially reducing emissions may lead to a relatively longer fumigant residence time in soil profile. The average 1,3-D concentrations in the soil-gas phase throughout the columns at 72 h were 0.8, 0.9, 1.0, 1.1, 1.0, 1.1, and 1.5 mg L^{-1} (standard deviations ranging from 0.1 to 0.3) for Treatments A–G, respectively. Fumigant concentrations at the 10-cm depth

for the first 24 h were similar for water seal and tarped treatments, implying that effects on pest control in that near-surface layer should be similar.

Soil Water Content and Residual Fumigant in Soils

Changes in soil water content by the end of the experiment in treated soil columns are shown in Fig. 4. Surface water application increased the soil water content in the soil columns to the 30-cm depth. The tarp on Treatment F did not appear to increase the stored water

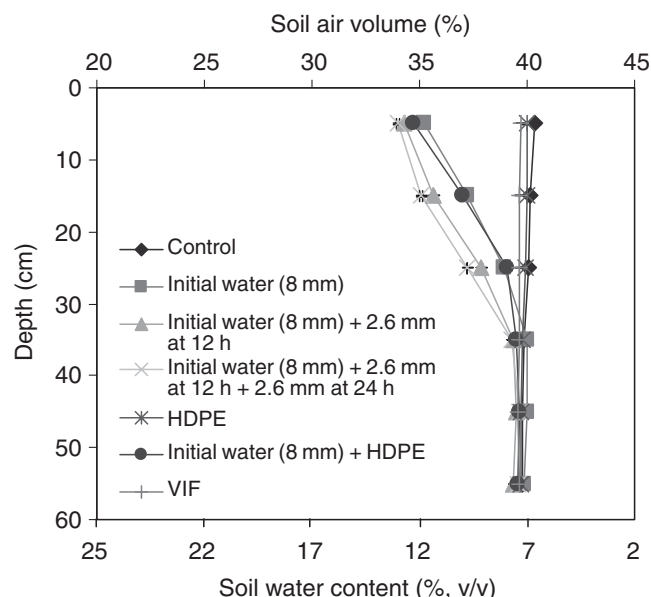


Fig. 4. Soil water content and soil air distribution in soil columns at the end of 2-wk experiment. Solid phase volume is estimated at about 50%. Horizontal bars are the range of duplicate values.

(i.e., substantially reduce surface evaporation) compared to the non-tarped columns. This may depend on the humidity condition in the laboratory during experiments. Soil water content increased near the soil surface (0–10 cm) as the amount of water added increased. The field capacity of this soil with a bulk density of 1.4 g cm^{-3} is estimated at about 24% (v/v). When no water was applied to the soil column, soil water content was relatively uniform (average of 7–8%, v/v) through the columns.

Total porosity of the soil columns was 47%, and volume of soil gas and water in the columns without water application were about 40% and 7% (v/v), respectively. The air volume in the top 10-cm soil was 34% in the three-time water application treatment and the corresponding water content was 13%. Although the water content would have been higher and the soil gas percentage lower just after water applications, it likely decreased to below its water holding capacity within a short time. This large volume of soil gas may partially explain why emission rates increased within a few hours of the application of water for this soil. The results imply that it is critical to maintain a continuous high water content in the soil surface to achieve maximum emission reduction. This also indicates that using surface water seals to reduce emissions in sandy soils with lower water holding capacity and quicker drainage than this soil will be a challenge.

Water application to the soil and its downward movement would have changed the volume of soil gas in the soil column as a function of time. This change was not monitored during the experimental period. By assuming water movement was very low after 3 d, 1,3-D in the soil-gas phase was estimated by integrating the product of air volume (using the phase distribution measured at the end of the experiment) and the fumigant concentrations in soil columns (Table 2). The control had the least total amount of 1,3-D at 72 and 168 h, but the differences

Table 2. Estimate of total mass of 1,3-D in the soil-gas phase from surface treatments.

Treatment†	1,3-D‡		
	72 h	168 h	336 h
	mg column ⁻¹		
Control	3.71 (0.63)	1.44 (0.26)	0.03 (0.04)
Initial water (8 mm)	3.40 (1.36)	1.56 (0.78)	0.04 (0.05)
Initial water (8 mm) + 2.6 mm at 12 h	3.54 (1.69)	1.69 (0.85)	0.04 (0.06)
Initial water (8 mm) + 2.6 mm at 12 h + 2.6 mm at 24 h	4.33 (0.01)	1.89 (0.36)	0.27 (0.06)
HDPE	4.33	1.63	0.22
Initial water (8 mm) + HDPE	4.34	1.90	0.28
VIF	6.79	4.33	1.90

† HDPE, high density polyethylene; VIF, virtually impermeable film.

‡ Values in parentheses are standard deviations of duplicate columns.

from other treatments were small except for the VIF tarp, which retained the highest amount of 1,3-D throughout the experimental period in the soil column.

At the end of the experiments, extractions of soil samples for liquid and solid phase 1,3-D showed that the extracted 1,3-D for all samples was low (less than 1 mg kg^{-1}) and there was no trend or difference in 1,3-D distribution in the soil columns (data not shown). The difference of total 1,3-D in soil among the treatments is shown in Table 3.

Degradation of 1,3-Dichloropropene in Soil

The fate of 1,3-D after injection into soil columns was estimated from cumulative emissions and data from soil gas and soil samples that were taken at the end of experiments (Table 3). The total amount of 1,3-D initially injected to the soil column was about 120 mg. The percentage of 1,3-D volatilized ranged from 10% (VIF) to 51% (control) of the total amount applied. The amount of 1,3-D in the soil-gas phase after 2 wk was very low, from non-detectable to about 2% (VIF tarp). The residual 1,3-D in soil liquid and solid phase were also small (3 to 5%). The residual 1,3-D in soils may be underestimated because, although procedures were followed to minimize loss, some losses of 1,3-D would have occurred during the process of removing the soil samples from the soil columns and transferring them into the extraction vials. The non-recovered fumigant (44 to 83%) is assumed

Table 3. Fate of 1,3-D 2 wk after application to soil columns.

Treatment†	Emission‡	Solid/liquid phase‡	Gas phase‡	Degradation§
(% of applied)¶				
Control	50.6 (1.6)	3.3 (1.6)	0.08 (0.11)	46.0
Initial water (8 mm)	46.1 (1.1)	2.6 (0.5)	0.02 (0.03)	51.2
Initial water (8 mm) + 2.6 mm at 12 h	44.5 (1.4)	3.5 (1.4)	0.03 (0.04)	52.1
Initial water (8 mm) + 2.6 mm at 12 h + 2.6 mm at 24 h	41.1 (3.8)	3.4 (1.4)	0.16 (0.14)	55.3
HDPE	44.9	3.8	0.18	51.2
Initial water (8 mm) + HDPE	38.0	4.6	0.23	57.1
VIF	9.9	5.4	1.56	83.1

† HDPE, high density polyethylene; VIF, virtually impermeable film.

‡ Measured.

§ Calculated by difference of measured from applied.

¶ Values in parenthesis are standard deviation for duplicate column measurements.

to have degraded in the soil. Degradation capacity in this soil is adequate to remove the majority of the fumigant if the fumigant is held in the soil long enough.

The values in Table 3 show that the primary fate of 1,3-D was either emission to the atmosphere or degradation in soil. By reducing emission rates, longer fumigant residence time in soil may be achieved and degradation of fumigants in soil may be promoted. This balance is important to establish the efficacious fumigant application rate although information is not yet adequate to quantify this balance. It is also unknown if increasing fumigant residence time in soil may increase the risk of fumigant leaching and ground water contamination.

The degradation values of 1,3-D in this study generally agree with reported data. The reported half-life of 1,3-D in soil can range from 4 to 43 d and averaged 11 d (Ajwa et al., 2003). Dungan et al. (2001) studied the effect of temperature, moisture, and organic amendment on 1,3-D degradation in a sandy loam soil and reported that the half-lives of both *cis*- and *trans*-1,3-D in unamended soil were 6.3 d at 20°C. The half-life decreased to about 2 d in soils amended with 5% composted steer manure. Gan et al. (1998b) found that the half-life of 1,3-D was between 5 and 7 d for two California soils at 20°C. The half-life of 1,3-D varies as soil temperature and water content change as these factors affect microbial activity and chemical reactions, the major degradation mechanisms. The role of these mechanisms varies depending on soil conditions. Microbial degradation of 1,3-D was found substantially depressed when the temperature was >30°C (Gan et al., 1998b). Hydrolysis of 1,3-D in deionized water is relatively rapid, with a half-life of 9.8 d at 20°C and the process is pH dependent (Guo et al., 2004a).

In our study, the VIF tarp treatment showed the highest amount of 1,3-D degraded although no water was added to the soil and the highest 1,3-D concentrations were retained in the soil-gas phase. The high degraded portion raises an interesting question on how 1,3-D or other fumigant degradation may respond to surface sealing and tarp treatments. Answers to this question can assist in prediction of fumigation efficacy.

Caution should be taken in applying the results from soil columns to the field conditions. The effectiveness of emission reducing treatments may vary under field conditions because water application, the soil surface, atmospheric conditions, and tarp condition will be less uniform and controlled than in the laboratory. Diurnal temperature changes and variable wind can affect emissions. Although the results cannot be directly applied to field conditions, the relative differences among treatments provide information on the potential of treatments that could be developed into effective practices in the field.

CONCLUSIONS

Surface water application can reduce 1,3-D emission more effectively than using standard HDPE tarp. High frequency, intermittent water application to maintain high surface soil water content is the key to maximize 1,3-D emission reductions. Using water is much less

expensive than using plastic tarp. Surface water application using sprinkler systems should have a potential to reduce 1,3-D emissions and be tested under field conditions.

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